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(54) POSITIVE ELECTRODE ACTIVE MATERIAL USING SURFACE-MODIFIED LITHIUM
NICKEL COMPOUND OXIDE, POSITIVE ELECTRODE MATERIAL, LITHIUM SECONDARY
BATTERY, AND MANUFACTURING METHOD FOR THE SURFACE-MODIFIED LITHIUM NICKEL
COMPOUND OXIDE

(57)Abstract:

PROBLEM TO BE SOLVED: To control rise of impedance generated by high
temperature conservation of a lithium secondary battery.

SOLUTION: This surface-modified lithium nickel compound oxide is used as
the positive electrode active material for the lithium secondary battery,
and it is manufactured by calcinating the lithium nickel compound oxide
after making a compound of a specific element among the elements of groups
4B-6B of the periodic table whose oxide has a melting point of 750°C or more

exist on the surface of a lithium nickel compound oxide.

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CLAIMS

[Claim(s)]

[Claim 1]

It is surface qualification lithium nickel complex oxide used as positive active material of a lithium secondary battery,
Surface qualification lithium nickel complex oxide characterized by being manufactured by calcinating said lithium nickel complex oxide after making the compound of the predetermined element whose melting point of the oxide

of said element is 750 degrees C or more among periodic-table 4B - 6B group's elements exist on the surface of lithium nickel complex oxide.

[Claim 2]

It is surface qualification lithium nickel complex oxide used as positive active material of a lithium secondary battery,

Surface qualification lithium nickel complex oxide characterized by the predetermined oxide or predetermined multiple oxide of an element whose melting point of the oxide of said element is 750 degrees C or more among periodic-table 4B - 6B group's elements existing on the surface of lithium nickel complex oxide.

[Claim 3]

Surface qualification lithium nickel complex oxide according to claim 1 or 2 said whose predetermined element is Nb or Ti.

[Claim 4]

The positive-electrode ingredient for lithium secondary batteries containing surface qualification lithium nickel complex oxide according to claim 1 to 3.

[Claim 5]

The lithium secondary battery which uses surface qualification lithium nickel complex oxide according to claim 1 to 3 as positive active material.

[Claim 6]

It is the manufacture approach of the surface qualification lithium nickel complex oxide used as positive active material of a lithium secondary battery,

The manufacture approach of the surface qualification lithium nickel complex oxide characterized by calcinating said lithium nickel complex oxide after making the compound of the predetermined element whose melting point of the oxide of said element it is an element belonging to periodic-table 4B - 6B group, and is 750 degrees C or more exist on the surface of lithium nickel complex oxide.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]

This invention relates to the lithium nickel complex oxide which embellished the front face with the compound of the predetermined element used as positive active material of a lithium secondary battery. Furthermore, it is related with the positive-electrode ingredient for lithium secondary batteries, positive electrode, and lithium secondary battery using the manufacture approach and said lithium nickel complex oxide of said lithium nickel complex oxide.

[0002]

[Description of the Prior Art]

A lithium secondary battery (in this specification, it may only be called a cell) is being adopted as a power source of electrical machinery and apparatus, such as a Personal Digital Assistant (Personal Digital Assistants, PDA), a portable personal computer, and a cellular phone.

[0003]

Since the technique which carries out the high-speed communication link of mass data like an animation by the cable or wireless between these Personal Digital Assistants and between cellular phones was established in recent years, the power consumption of these electrical machinery and apparatus tends to become large. For this reason, for the cell capacity of the lithium secondary battery used as a power source to be also higher, and to carry out is desired.

As positive active material used for these lithium secondary batteries, promising ** of the lithium transition-metals multiple oxide is carried out. Since the lithium nickel complex oxide which uses nickel as transition metals also in these lithiums transition-metals multiple oxide has a large cell capacity per unit weight, it attracts attention as useful positive active material. The lithium secondary battery using lithium nickel complex oxide as positive active material can actually secure high capacity now by making a charge electrical potential difference more than 4V.

[0004]

However, the cell engine performance may fall and the cell using lithium nickel complex oxide as positive active material has the technical problem that he wants to make higher thermal stability of lithium nickel complex oxide, when used or saved under hot environments.

In order to solve such a technical problem, there is a technique of making LiMO₂ (M, nickel or nickel and in addition to this one or more sorts of transition-metals elements) containing V (vanadium) compound (patent

reference 1).

[0005]

[Patent reference 1]

JP, 2002-260660, A

[0006]

[Problem(s) to be Solved by the Invention]

The technical problem that he wants to make higher thermal stability of lithium nickel complex oxide occurs as above-mentioned.

this invention person is examining embellishing the front face of lithium nickel complex oxide with the compound of various elements, in order to raise the thermal stability of lithium nickel complex oxide. An aim raises the thermal stability of lithium nickel complex oxide by this performing surface qualification with the compound of a predetermined element, and controlling the reaction in the front face of lithium nickel complex oxide.

[0007]

And according to examination of this invention person, it became clear that the thermal stability of lithium nickel complex oxide did not necessarily become high even if it uses a vanadium compound. As a result of pursuing the cause, it became clear that this was because the melting point of the banazin san ghost (V205) in the inside of atmospheric air is as low as 690 degrees C.

Lithium nickel complex oxide touches the electrolytic solution in a cell. For this reason, to perform surface qualification of lithium nickel complex oxide, it is necessary to strengthen with the bonding strength (adhesive strength) of a surface modulator and lithium nickel complex oxide so that the modulator (the matter which exists in the front face of surface qualification lithium nickel complex oxide may be called surface modulator in this specification) which exists in a front face may not dissolve into the electrolytic solution. For this reason, this invention person is strengthening the bonding strength of lithium nickel complex oxide and a surface modulator by calcinating, after making the qualification ingredient which is a raw material of a surface modulator on the surface of lithium nickel complex oxide exist, obtaining the oxide or the multiple oxide of the above-mentioned qualification ingredient, and making this into a surface modulator.

[0008]

however, the temperature of baking in order to heighten the above-mentioned bonding strength, using a vanadium compound as a qualification ingredient — more — high — carrying out (for example, 700-800 degrees C) — it dissolves on a lithium-nickel-complex-oxide front face, and the interior

of lithium nickel complex oxide is permeated, or the surface modulator (V205 which is especially the oxide of vanadium) generated by baking flows and falls from a lithium-nickel-complex-oxide front face, and qualification on the front face of lithium nickel complex oxide is not fully performed.

[0009]

[Means for Solving the Problem]

Therefore, the purpose of this invention is by using a qualification ingredient which exists in stability on a lithium-nickel-complex-oxide front face in the state of a surface modulator to obtain the lithium nickel complex oxide which has high thermal stability.

The lithium secondary battery with which this invention person etc. uses lithium nickel complex oxide as positive active material in view of the above-mentioned purpose was examined wholeheartedly that the stability in an elevated temperature should be improved, maintaining a high capacity which is the advantage of lithium nickel complex oxide.

[0010]

Consequently, when using the compound of the element with which the melting point of the oxide in the inside of atmospheric air serves as near temperature or the temperature beyond it which performs baking with a qualification ingredient and lithium nickel complex oxide among periodic table 4B - 6B group's elements as a qualification ingredient, the oxide or the multiple oxide (surface modulator) of the above-mentioned element obtained by baking existed in the lithium-nickel-complex-oxide front face stably, and found out that the high lithium nickel complex oxide of thermal stability could be obtained. And the lithium secondary battery which uses such lithium nickel complex oxide as positive active material completed header this invention for the thing of an impedance rise controlled also in elevated-temperature preservation and elevated-temperature cycle operation.

[0011]

That is, the first summary of this invention is surface qualification lithium nickel complex oxide used as positive active material of a lithium secondary battery, and after making the compound of the predetermined element whose melting point of the oxide of said element is 750 degrees C or more among periodic-table 4B - 6B group's elements exist on the surface of lithium nickel complex oxide, it consists in the surface qualification lithium nickel complex oxide characterized by being manufactured by calcinating said lithium nickel complex oxide.

[0012]

And the second summary of this invention is surface qualification lithium

nickel complex oxide used as positive active material of a lithium secondary battery, and consists in the surface qualification lithium nickel complex oxide characterized by the predetermined oxide or predetermined multiple oxide of an element whose melting point of the oxide of said element is 750 degrees C or more among periodic-table 4B - 6B group's elements existing on the surface of lithium nickel complex oxide.

[0013]

Moreover, the third summary of this invention is the manufacture approach of the surface qualification lithium nickel complex oxide used as positive active material of a lithium secondary battery, and after making the compound of the predetermined element whose melting point of the oxide of said element it is an element belonging to periodic-table 4B - 6B group, and is 750 degrees C or more exist on the surface of lithium nickel complex oxide, it consists in the manufacture approach of the surface qualification lithium nickel complex oxide characterized by calcinating said lithium nickel complex oxide.

[0014]

Furthermore, the summary of others [this invention] consists in the lithium secondary battery characterized by using as positive active material the positive-electrode ingredient for lithium secondary batteries characterized by containing said surface qualification lithium nickel complex oxide, and said surface qualification lithium nickel complex oxide. In addition, in this invention, the compound of the element whose melting point of the oxide of said element is 750 degrees C or more is called a "qualification ingredient" by the element of periodic-table 4B - 6B group who exists lithium nickel complex oxide in the lithium-nickel-complex-oxide front face "before calcinating." On the other hand, said predetermined oxide or predetermined multiple oxide of an element etc. which exists in the lithium-nickel-complex-oxide front face after baking is called a "surface modulator." A qualification ingredient and a surface modulator may be different (although the matter itself does not change with baking, when the adhesive strength of the matter and lithium nickel complex oxide becomes strong) matter, when it is the same ingredient (when a qualification ingredient reacts by baking, it becomes a surface modulator and adhesive strength with lithium nickel complex oxide becomes strong).

[0015]

[Embodiment of the Invention]

[1] Surface qualification lithium nickel complex oxide and its process
After the positive active material of the lithium secondary battery used

for this invention makes the compound of the predetermined element whose melting point of the oxide of said element is 750 degrees C or more among periodic-table 4B - 6B group's elements exist on the surface of lithium nickel complex oxide, it is characterized by being manufactured by calcinating said lithium nickel complex oxide.

(A) Meaning using the surface qualification lithium nickel complex oxide of this invention

this invention person considered aggravation of the high temperature oxidation stability of a lithium secondary battery which used lithium nickel complex oxide, and especially an impedance rise of the lithium secondary battery generated by elevated-temperature preservation that the reactivity in the front face of lithium nickel complex oxide is the cause. That is, since the part to which basicity becomes high as compared with other lithium transition-metals multiple oxides, and its reactivity became high, when lithium nickel complex oxide became an elevated temperature, the solvent contained in the electrolytic solution carried out oxidative degradation on the lithium-nickel-complex-oxide front face, and formed the coat, and it surmised that it was the factor which this coat makes generate an impedance rise.

[0016]

When the lithium secondary battery using lithium nickel complex oxide was saved at an elevated temperature, or when this invention person covered the front face of lithium nickel complex oxide with a certain ingredient under the above-mentioned guess, or made it react with a certain ingredient, and surface activity was held down, and it carried out by repeating charge and discharge in an elevated temperature, I thought that the impedance rise could be controlled. However, said covering material or a reaction ingredient must be an ingredient which can control the stability at the time of elevated-temperature preservation, without spoiling cell properties, such as an impedance in the usual condition of a lithium secondary battery of having used lithium nickel complex oxide, cell capacity, a rate property, and a low-temperature property. this invention person etc. found out that it was suitable to use the compound of periodic-table 4B which forms nickel which exists in lithium nickel complex oxide, and a stable compound - 6B group element as a qualification ingredient, as a result of examining such an ingredient wholeheartedly.

[0017]

On the other hand, in this invention, it is necessary to heighten the bonding strength (adhesive strength) of a surface modulator and lithium nickel complex oxide so that a surface modulator may not be eluted in the

electrolytic solution in a cell. For this reason, this is calcinated after making the compound of the above-mentioned periodic-table 4B - 6B group element which is a qualification ingredient exist in a lithium-nickel-complex-oxide front face. By obtaining the oxide (periodic table 4 the oxide of B - 6B group element being formed) or multiple oxide (periodic table 4 oxide of the two or more elements and oxygen containing B - 6B group element) of a qualification ingredient, and making this into a surface modulator The bonding strength (adhesive strength) of a surface modulator and lithium nickel complex oxide is heightened.

[0018]

However, if such baking processing is performed, it will become difficult among the compounds of periodic table 4B - 6B group element suitable as a qualification ingredient to use a vanadium compound. This is because V2O5 (melting point: 690 degrees C) with the low melting point which has a vanadium compound calcinated dissolves, flow from a lithium-nickel-complex-oxide front face, and it falls, or the interior of lithium nickel complex oxide is permeated and the amount of vanadium oxides on a lithium-nickel-complex-oxide front face cannot fully be secured, if it calcinates at the temperature of 700 degrees C or more in order to heighten the above-mentioned bonding strength (adhesive strength). It is one side and is periodic-table 4B.

- TiO2 (melting point: 1843 degrees C) and ZrO2 which are the oxide of 6B group element (melting point)

: 2715 degrees C, HfO2 (melting point: 2758 degrees C) and Nb2O5 (melting point: 1485 degrees C), Ta2O5 (melting point: 1872 degrees C), Cr2O3 (melting point: 2300 degrees C), and MoO3 (melting point: 795 degrees C) and WO3 (melting point: 1413 degrees C) have the fully high melting point respectively, and a problem like the above-mentioned V2O5 does not occur.

[0019]

For this reason, in this invention, the compound of the element whose melting point of the oxide of said element is near burning temperature or the temperature beyond it among periodic-table 4B - 6B group's elements is used as a qualification ingredient. The temperature at the time of baking can make a surface modulator certainly exist in a

lithium-nickel-complex-oxide front face here, if the melting point of oxide uses a thing 750 degrees C or more since it is an elevated temperature comparatively although it changes with classes of qualification ingredient to be used.

[0020]

In addition, not only when the front face of said lithium nickel complex

oxide is only covered by calcinating this after making a predetermined compound exist in the front face of lithium nickel complex oxide but the case where made said predetermined compound made to exist react on a lithium-nickel-complex-oxide front face by baking, and a lithium-nickel-complex-oxide front face is embellished shall be included with the "surface qualification lithium nickel complex oxide" in this invention.

[0021]

As above-mentioned, on the surface of lithium nickel complex oxide, the surface qualification lithium nickel complex oxide of this invention is manufactured by calcinating this, after making the compound of periodic-table 4B - 6B group elements other than vanadium (Ti, Zr, Hf, Nb, Ta, Cr, Mo, and W) exist. This manufacture approach etc. is explained in full detail below.

(B) Lithium nickel complex oxide

The lithium nickel complex oxide used in this invention is an oxide which contains a lithium and nickel at least. As lithium nickel complex oxide, lithium nickel complex oxide like LiNiO_2 which has the layer structures, such as $\alpha\text{-NaFeO}_2$ structure, for example is desirable. As a concrete presentation, LiNiO_2 and $\text{LiNi}_{2/3}\text{O}_2$ grade can be mentioned, for example. In this case, lithium nickel complex oxide may permute a part of site which nickel occupies by elements other than nickel. The stability of the crystal structure can be raised by permuting a part of nickel site by other elements, and since the capacity fall which some nickel elements at the time of carrying out repeat charge and discharge move to Li site, and it generates is controlled, a cycle property also improves. Furthermore, in order that the exoergic initiation temperature of DSC (Differential Scanning Calorimetry: differential scanning calorimetry) may shift to an elevated-temperature side by permuting a part of nickel site by elements other than nickel, the thermal-run-away reaction of lithium nickel complex oxide when the temperature of a cell rises is also controlled, and it leads to improvement in the safety at the time of elevated-temperature preservation as a result.

[0022]

As this element at the time of elements other than nickel permuting a part of site which nickel occupies (it is hereafter written as a permutation element), aluminum, Ti, V, Mn, Co, Li, Cu, Zn, Mg, Ga, Zr, etc. are mentioned, for example. Of course, nickel site may be permuted by two or more sorts of other elements. aluminum, Ti, Co, Li, Mg, Ga, and Mn are mentioned preferably, and aluminum, Ti, Co, and Mn are mentioned still more preferably.

The improvement effect of a cycle property and safety becomes large by permuting some nickel elements from aluminum, Ti, Co, and Mn.

[0023]

the case where a permutation element permutes nickel site -- the rate -- usually -- more than 2.5 mol % of nickel element -- desirable -- more than 5 mol % -- it is -- usually -- less than [of nickel element / 50 mol %] -- it is less than [30 mol %] preferably. If many [if there are too few permutation rates, improvement effects, such as a cycle property, may not be enough, and / too], the capacity at the time of making it a cell may fall.

[0024]

In addition, in the above-mentioned presentation, you may have indeterminate ratio nature, such as a little oxygen deficiency. Moreover, a part of oxygen site may be permuted by sulfur or the halogen. As for lithium nickel complex oxide, in this invention, it is desirable that no permuting or nickel site expressed with the following general formula (1) is the compound permuted by Co and the predetermined element.

[0025]

$\text{Li}\alpha\text{NiXCoYMZO}_2\text{-}\beta\text{Fb}\alpha$ (1)

α is a number which changes with the situations of the charge and discharge within a cell among a general formula (1), and α is 0.95 or more more preferably and, on the other hand, is usually usually [zero or more] 1.08 or less preferably 1.1 or less 0.3 or more. A repeat charge-and-discharge property (in this specification, it may be called a cycle property) becomes good, maintaining this range, then high capacity. The balance of 0.95 or more [then], and a capacity and a cycle property is maintained more at fitness especially in α .

[0026]

X is 0.7 or more more preferably and, on the other hand, is 0.9 or less preferably one or less 0.5 or more 0.1 or more. It becomes it is high and good [***** and a cycle property] about this range, then capacity. Although it is desirable that it is close to 1 as for X, when a cycle property is taken into consideration from the point of capacity, especially a good thing is making X or less [0.7 or more] into 0.9.

[0027]

Y -- zero or more -- desirable -- 0.05 or more -- more -- desirable -- 0.1 or more -- it is -- on the other hand -- it is 0.3 or less more preferably 0.4 or less 0.9 or less. The safety as a lithium secondary battery also comes to be secured, keeping this range, then a cycle property good.

Z -- zero or more -- desirable -- 0.01 or more -- more -- desirable -- 0.1

or more — it is — on the other hand — it is 0.05 or less more preferably 0.2 or less 0.8 or less. The safety as a lithium secondary battery can be secured now, without dropping this range, then cell capacity.

[0028]

In addition, although X, above-mentioned Y, and above-mentioned Z fill the relation of $0.9 \leq X+Y+Z \leq 1.1$, they are usually 1.0.

beta is 0.01 or more preferably and, on the other hand, is 0.1 or less preferably 0.5 or less zero or more. Since this range, then fluorine come to be incorporated by the crystal of lithium nickel complex oxide, the safety as a lithium secondary battery can be made high.

[0029]

M is at least one chosen from the group which consists of Li, Mg, calcium, Sr, Cu, Zn, aluminum, Ga, Ti, Zr, V, Nb, Ta, Cr, Mo, W, Mn, and Fe. By setting M to at least one of the above-mentioned elements, the safety as a lithium secondary battery can be made high now. It is setting M to at least one chosen from the group which consists of Li, Mg, aluminum, Ga, Ti, Nb, Cr, Mo, Mn, and Fe preferably. There is not only an advantage that nickel and an ionic radius are easy to permute by near and nickel, but these elements have the advantage of being easy to receive also industrially. It is the thing of Mn, Mg, aluminum, and Ga set to any one at least about M still more preferably. It is because especially these elements are easy to come to hand industrially. Especially a desirable thing is setting M to aluminum and Mn. aluminum and Mn have an advantage with cheap cost.

[0030]

The specific surface area of the lithium nickel complex oxide used by this invention is more than 0.3m²/g more preferably, and is below 0.7m²/g below 1m²/g below 10m²/[of usual] g more than 0.1m²/g preferably more than 0.01m²/[of usual] g. It becomes without the charge-and-discharge property in the high current by the lithium ion of the site [an intercalation and] which carries out a day intercalation decreasing getting worse specific surface area controlling effectively this range, then the generation of gas at the time of elevated-temperature preservation. Measurement of specific surface area follows a BET adsorption method.

[0031]

The description of lithium nickel complex oxide is usually fine particles in ordinary temperature normal relative humidity (25 degrees C / 50%RH), and it is common that it is in the condition of the primary particle of the diameter of a granule having condensed and having formed the aggregated particle. And 100 micrometers or less 50 micrometers or less are 20 micrometers or less most preferably still more preferably usually

preferably [the secondary / an average of / particle size of this aggregated particle is usually desirable 0.1 micrometers or more, and 0.2 micrometers or more 0.3 micrometers or more are 0.5 micrometers or more most preferably still more preferably, and] 300 micrometers or less. The high safety as a lithium secondary battery can be maintained controlling the above-mentioned range, then cycle degradation of a cell for secondary [an average of] particle size. Moreover, since the internal resistance value of a cell can be made small, a cell output can also be enlarged.

(C) The compound of periodic-table 4B - 6B group element with which the melting point of an oxide becomes 750 degrees C or more, and said element (qualification ingredient)

As a periodic-table 4B - 6B group element with which the melting point of an oxide becomes 750 degrees C or more, Ti, Zr, Hf, Nb, Ta, Cr, Mo, and W are mentioned. Therefore, what is necessary is just to use the compound of the element of either Ti, Zr, Hf, Nb, Ta, Cr, Mo and W as a qualification ingredient in this invention. Also in these compounds, as a qualification ingredient, the thing of Nb compound, Ta compound, and Ti compound for which either is used at least is desirable, and especially the thing for which Nb compound and/or Ti compound are used is desirable. It is because this tends to form a compound with as stable Nb compound, Ta compound, and Ti compound as nickel and Nb compound and Ti compound tend to form especially nickel and a stable compound.

[0032]

although especially a limit is not carried out for Nb compound — desirable one — niobium oxide and niobium fluoride, chlorination niobium, 3 chlorination niobium oxide, and bromination — it is using at least one chosen from the group which consists of niobium, iodation niobium, oxalic acid niobium ammonium, and oxalic acid hydrogen niobium. These Nb(s) compound is a solid-state in ordinary temperature normal relative humidity (25 degrees C / 50%RH).

[0033]

niobium fluoride with the melting point or decomposition temperature lower than 800 degrees C whose more desirable Nb compounds used as these qualification ingredient are the general decomposition temperature of lithium nickel complex oxide, chlorination niobium, and bromination — they are niobium and iodation niobium. Moreover, it is also desirable to use niobium oxide from a viewpoint which makes high stability of the surface qualification lithium nickel complex oxide at the time of elevated-temperature preservation.

[0034]

Also in the above-mentioned Nb compound, niobium oxide is the most desirable in the point which can make high stability of the surface qualification lithium nickel complex oxide at the time of elevated-temperature preservation.

although especially a limit is not carried out for Ti compound -- titanium oxide and titanium fluoride, a titanium chloride, and bromination -- it is desirable that it is at least one chosen from the group which consists of titanium, iodation titanium, 2 chlorination titanium oxide, a titanium sulfide, sulfuric-acid titanium, oxidization sulfuric-acid titanium, selenium-ized titanium, nitric-acid titanium, hexafluoro titanic-acid ammonium, bis(cyclopentadienyl) titanium, tetra-benzyl titanium, and titanium oxalate ammonium. These Ti compound is a solid-state in ordinary temperature normal relative humidity (25 degrees C / 50%RH).

[0035]

a titanium chloride and bromination with the melting point or decomposition temperature lower than the decomposition temperature of 800 degrees C with lithium nickel complex oxide common [more desirable one in these Ti compound] -- they are titanium, iodation titanium, 2 chlorination titanium oxide, sulfuric-acid titanium, oxidization sulfuric-acid titanium, hexafluoro titanic-acid ammonium, tetra-benzyl titanium, and titanium oxalate ammonium. Moreover, it is also desirable to use titanium oxide for the stability of the surface qualification lithium nickel complex oxide at the time of elevated-temperature preservation from a viewpoint highly.

[0036]

Also in the above-mentioned Ti compound, titanium oxide is the most desirable in the point which can make high stability of the surface qualification lithium nickel complex oxide at the time of elevated-temperature preservation.

Periodic table 4 The compound of B - 6B group element is secondary [the] although it is powdered at ordinary temperature normal relative humidity. 5 micrometers or less of particle size of a particle are usually 1 micrometer or less preferably. Although the diameter of an aggregated particle of the above-mentioned compound is more desirable as it is small, it is usually set to 0.01 micrometers or more from a viewpoint which carries out surface qualification of lithium nickel complex oxide to homogeneity.

(D) The approach in which a qualification ingredient is made to exist on the surface of lithium nickel complex oxide

A qualification ingredient (periodic table 4 compound of an element with which the melting point of an oxide becomes 750 degrees C or more among B - 6B group elements) is made to exist on the surface of lithium nickel

complex oxide in the manufacture approach of the surface qualification lithium nickel complex oxide of this invention.

[0037]

the rate of a qualification ingredient of as opposed to lithium nickel complex oxide at this time -- usually -- more than 0.001wt% -- desirable -- more than 0.01wt% -- more -- desirable -- more than 0.05wt% -- it carries out to more than 0.1wt% preferably especially. The reaction of the electrolytic solution and lithium nickel complex oxide under this range, then hot environments can be controlled effectively. the rate of a qualification ingredient of as opposed to lithium nickel complex oxide on the other hand -- usually -- less than [20wt%] -- desirable -- less than [10wt%] -- more -- desirable -- less than [5wt%] -- especially -- desirable -- less than [3wt%] -- it is less than [1wt%] most preferably. The fall of the cell capacity by embellishing the above-mentioned range, then the front face of lithium nickel complex oxide too much and the fall of the output by the increment in resistance can be controlled now.

[0038]

Moreover, in this invention, it is desirable to make a qualification ingredient the particle front face of lithium nickel complex oxide exist in homogeneity. For this reason, it is desirable that the diameter of a primary particle or the diameter of an aggregated particle of said qualification ingredient is smaller than the diameter of an aggregated particle of lithium nickel complex oxide. When the diameter of a primary particle or the diameter of an aggregated particle of a qualification ingredient becomes large to the diameter of an aggregated particle of lithium nickel complex oxide, a qualification ingredient does not adhere to a lithium-nickel-complex-oxide front face partially, and uniform qualification has a possibility that it cannot do. When the second [an average of] particle diameter of lithium nickel complex oxide is set to 1 from such a viewpoint, the ratio of the first [an average of] particle diameter of the qualification ingredient to this or the second [an average of] particle diameter is usually 0.1 or less preferably 0.5 or less. Although the first [an average of] particle diameter or the second [an average of] particle diameter of a qualification ingredient is more desirable as it is small to the second [an average of] particle diameter of lithium nickel complex oxide, actually, 0.001 or more are usually the above-mentioned particle-size ratio.

[0039]

It is more desirable to use a wet method, for example as an approach of making a qualification ingredient existing in the particle front face of

lithium nickel complex oxide, if industrial productivity is taken into consideration although a wet method, dry process, or a gaseous-phase method can be used.

(D-1) Wet method

A wet method is an approach of making a qualification ingredient existing in the front face of said lithium nickel complex oxide, by dissolving or distributing a qualification ingredient to a solvent, supplying lithium nickel complex oxide to this, and contacting a qualification ingredient and lithium nickel complex oxide in a solvent. Without using a qualification ingredient so much, a wet method can process a lithium-nickel-complex-oxide front face to homogeneity, and has an advantage with high productive efficiency.

[0040]

As a solvent in the case of making a solvent dissolve or distribute the compound of an element with which the melting point of an oxide becomes 750 degrees C or more among periodic-table 4B - 6B group elements which are qualification ingredients, an acetone, a methanol, ethanol, a hexane, a cyclohexane, toluene, water, an oxalic acid water solution, etc. can be mentioned, for example. The above-mentioned solvent may use plurality together. Here, as the solution or dispersion liquid of a compound of an element with which the melting point of an oxide becomes 750 degrees C or more among periodic-table 4B - 6B group elements, the niobium oxide sol which made the solvent dissolve or distribute niobium oxide, and the titanium oxide sol which made the solvent distribute titanium oxide can be mentioned, for example. Since these sols can come to hand also industrially and can process a lithium-nickel-complex-oxide front face with a wet method on ***, the uniform surface qualification of them is attained.

[0041]

If it is distributed equipment with which the function which can carry out evaporation to dryness of this in reduced pressure was added further as equipment which makes a solvent distribute a qualification ingredient that what is necessary is just kneading and equipment which can be agitated, applying heat, in addition, it is desirable. As such equipment, a rotary evaporator can be mentioned in laboratory. Moreover, if a dispersant is used in case a solvent is made to distribute a qualification ingredient, a uniform slurry will be obtained and it will become easy to make a lithium-nickel-complex-oxide front face a qualification ingredient adhere to homogeneity. As a dispersant, a surfactant can be mentioned, for example.

[0042]

As equipment which makes a qualification ingredient exist in a lithium-nickel-complex-oxide front face, the equipment to which the solution or dispersion liquid which the compound of an element with which the melting point of an oxide becomes 750 degrees C or more among periodic-table 4B which is a qualification ingredient - 6B group element contains can be contacted can be mentioned, for example, moving the particle of lithium nickel complex oxide. Industrially, the equipment to which spray the solution or distributed solution (slurry) containing the compound of an element with which the melting point of an oxide becomes 750 degrees C or more among periodic-table 4B - 6B group elements, and it is made to adhere using a spray etc., for example, a pan coating machine, a spray dryer, etc. can be mentioned, making lithium-nickel-complex-oxide fine particles flow.

(D-2) Dry process

Dry process is an approach of making a qualification ingredient existing in the particle front face of lithium nickel complex oxide, by contacting solid-state-like a qualification ingredient and a lithium-nickel-complex-oxide particle (solid-state), without minding a solvent, and mixing these solid-states-like a qualification ingredient and a lithium-nickel-complex-oxide particle.

(D-3) Gaseous-phase method

A gaseous-phase method means the approach of making a qualification ingredient existing in a lithium-nickel-complex-oxide particle front face, by contacting a gas-like qualification ingredient to a solid-state-like lithium-nickel-complex-oxide particle. A gaseous-phase method has the advantage which is easy to make the compound of an element with which the melting point of oxide becomes 750 degrees C or more among periodic-table 4B which is a qualification ingredient - 6B group element exist in homogeneity on the surface of lithium nickel complex oxide.

[0043]

When using a gaseous-phase method, and heating etc. carries out a qualification ingredient, it is desirable to make it the shape of a gas, to contact this to lithium nickel complex oxide, and to make a qualification ingredient exist on the surface of lithium nickel complex oxide.

As a concrete approach, a lithium-nickel-complex-oxide particle is put in into a furnace, and it is a gas-like qualification ingredient (the compound of an element with which the melting point of an oxide becomes 750 degrees C or more among 6[periodic-table 4B -] B group elements: for example) to this. The niobium fluoride which will be evaporated if it heats, chlorination niobium, 3 chlorination niobium oxide, bromination — niobium,

iodation niobium, and titanium fluoride, a titanium chloride, and bromination — the approach of blowing titanium and an iodation titanium steam — Both the compounds of an element with which the melting point of an oxide becomes 750 degrees C or more among periodic-table 4B which is solid-state-like lithium nickel complex oxide and a qualification ingredient - 6B group element are installed in a furnace, a furnace is heated and the compound of periodic table 4B - 6B group element is evaporated — making — a lithium-nickel-complex-oxide front face — adhesion **** — an approach [like] can be mentioned.

(E) Baking

In the manufacture approach of the surface qualification lithium nickel complex oxide of this invention, this is calculated, after making the compound of an element with which the melting point of oxide becomes 750 degrees C or more among periodic-table 4B which is a qualification ingredient - 6B group element exist in a lithium-nickel-complex-oxide front face. The oxide of a qualification ingredient or the multiple oxide of a qualification ingredient can be made to exist in a lithium-nickel-complex-oxide front face stably by calcinating now. Here, the multiple oxide of a qualification ingredient means the oxide of at least 1 of Ti, Zr, Hf, Nb, Ta, Cr, Mo, and W (periodic table 4 element with which the melting point of an oxide becomes 750 degrees C or more among B - 6B group elements), the element of further others, and oxygen.

[0044]

Especially the temperature that calcinates is not restricted. For example, when making a qualification ingredient exist in a lithium-nickel-complex-oxide front face using the above-mentioned gaseous-phase method, burning temperature should just be beyond the temperature that a qualification ingredient evaporates.

On the other hand, as for burning temperature, it is desirable that it is below the decomposition temperature of lithium nickel complex oxide. Since lithium nickel complex oxide itself decomposes when burning temperature is said more than decomposition temperature, it may become difficult to make a qualification ingredient adhere to a lithium-nickel-complex-oxide front face firmly. It is desirable to use Nb compound or Ti compound as a compound of an element with which the melting point of an oxide becomes 750 degrees C or more from such a viewpoint among periodic-table 4B which is a qualification ingredient - 6B group element.

[0045]

Here, the decomposition temperature of lithium nickel complex oxide changes with the presentations. In getting it blocked, for example, permuting a

part of nickel site with Co or aluminum, the decomposition temperature of lithium nickel complex oxide becomes high, so that there are many amounts of permutations. Moreover, when lithium nickel complex oxide is the presentation of $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.4}\text{Mn}_{0.4}]\text{O}_2$, in order to compound lithium nickel complex oxide at 900 degrees C, it is desirable to perform baking with the compound of periodic-table 4B - 6B group element below 900 degrees C. In the presentation ($\text{LiNi}_{0.82}\text{Co}_{0.15}\text{Aluminum}_{0.0302}$) used also in the below-mentioned example, since it is thought that near 780 degree C is decomposition temperature (temperature to which the cell engine performance begins to fall at least), baking with the compound of periodic-table 4B - 6B group element is performed below 780 degrees C. [0046]

Moreover, when [for example,] niobium oxide is used as a compound of an element with which the melting point of oxide becomes 750 degrees C or more among periodic-table 4B which is a qualification ingredient - 6B group element, the melting point of niobium oxide itself -- very much -- being high (1485 degrees C), since decomposition temperature will become 800 degrees C or less if this is distributed to a solvent and it is a niobium oxide sol If the front face of lithium nickel complex oxide is processed by the niobium oxide sol using a wet method even if it calcinates at 500-780 degrees C which is an optimum-temperature field for lithium nickel complex oxide ($\text{LiNi}_{0.82}\text{Co}_{0.15}\text{Aluminum}_{0.0302}$) -- the front face of lithium nickel complex oxide -- the multiple oxide of niobium oxide or niobium -- homogeneity -- and it can embellish now firmly. However, if at least 500 degrees C or less of time amount are spent, it will be thought to some extent that a reaction progresses.

[0047]

As mentioned above, generally [generally / although it is difficult to appoint a burning-temperature field uniquely in order to be dependent on the presentation of the class of qualification ingredient which uses burning temperature, description, and lithium nickel complex oxide etc. / 400 degrees C or more 500 degrees C or more are 656 degrees C or more more preferably, and] on the other hand, 850 degrees C or less 780 degrees C or less are 750 degrees C or less more preferably. A surface modulator comes to be firmly embellished by the lithium-nickel-complex-oxide front face, this temperature requirement, then the temperature field below the decomposition temperature of lithium nickel complex oxide being secured.

[0048]

Although what is necessary is just to perform the ambient atmosphere at the time of performing baking with a compound of an element and lithium

nickel complex oxide from which the melting point of oxide becomes 750 degrees C or more among periodic-table 4B which is a qualification ingredient - 6B group element in atmospheric air, calcinating in an oxygen ambient atmosphere is desirable. If it calcinates in an oxygen ambient atmosphere, the high oxide and high multiple oxide of the melting point will become are easy to be formed.

[0049]

Since lithium nickel complex oxide itself may deteriorate on the other hand in the case of baking when a lot of carbon dioxide gas and moisture mix into a firing environments, as for carbon dioxide gas and the moisture in a firing environments, lessening as much as possible is desirable.

It depends on burning temperature for the firing time at the time of performing baking with a qualification ingredient and lithium nickel complex oxide. That is, since it is the problem of a reaction rate whether the compound and lithium nickel complex oxide of an element with which the melting point of oxide becomes 750 degrees C or more among periodic-table 4B which is a qualification ingredient - 6B group element in the case of baking fully react, when burning temperature is high, there is little firing time and it ends, and when burning temperature is low, on the other hand, the need of taking long firing time comes out.

[0050]

Moreover, it depends for the firing time at the time of performing baking with a qualification ingredient and lithium nickel complex oxide on the scale which performs burning temperature and baking. That is, it ends with 500 degrees C in about 2 hours, and case [like 1kg scale], it is needed at 500 degrees C with laboratory level like 100g scale for about 6 hours. In addition, since a certain amount of time amount will be needed by the time the temperature of the temperature of the furnace which calcinates, a qualification ingredient, and lithium nickel complex oxide becomes almost the same in producing industrially, when deciding firing time, it must be cautious also of the scale which calcinates enough.

[0051]

It depends for the firing time at the time of performing baking with a compound of an element and lithium nickel complex oxide from which the melting point of oxide becomes 750 degrees C or more among periodic-table 4B which is furthermore a qualification ingredient - 6B group element also on the compound of periodic-table 4B - 6B group element to be used. For example, since decomposition temperature can be lowered by making it a niobium oxide sol when using high-melting niobium oxide as a compound of periodic table 4B - 6B group element If the front face of lithium nickel

complex oxide is processed with a wet method using a niobium oxide sol firing time -- usually -- 1 minutes or more -- desirable -- 30 minutes or more -- more -- desirable -- 1 hours or more -- it can do -- on the other hand -- usually -- it can be 6 or less hours now more preferably for 12 or less hours for 72 or less hours.

[0052]

in addition, although the thing with the short time amount which it was alike and was exceeded does not have firing time when productivity is taken into consideration, whether the reaction of lithium nickel complex oxide and the compound of periodic-table 4B - 6B group element is completed also has the field which changes also according to the mixed state. Therefore, when the upper limit of firing time is decided from the productivity and burning temperature of surface qualification lithium nickel complex oxide, for example, it makes burning temperature into 700 degrees C, if firing time is made into 24 hours, it will be thought that it is enough.

[0053]

The surface qualification lithium nickel complex oxide of this invention can be obtained through the ingredient and process which are shown in (B) - (E) above.

(F) Surface qualification lithium nickel complex oxide

In the surface qualification lithium nickel complex oxide of this invention, the predetermined oxide or predetermined multiple oxide of an element (Ti, Zr, Hf, Nb, Ta, Cr, Mo, and W) whose melting point of the oxide of said element is 750 degrees C or more among periodic-table 4B - 6B group's elements exists on the surface of lithium nickel complex oxide.

[0054]

In a lithium-nickel-complex-oxide front face, although matter other than the above-mentioned oxide or a multiple oxide may also exist, if the oxide and multiple oxide of the specified quantity exist, the effectiveness of this invention will fully be demonstrated. And it is desirable to make effectiveness of this invention into the range as [of the qualification ingredient to lithium nickel complex oxide] explained comparatively (wt%) above (D), since it is fully demonstrated.

[0055]

When a qualification ingredient is the oxide of at least one element of Ti, Zr, Hf, Nb, Ta, Cr, Mo, and W, as for a surface modulator, these oxides remain as they are, or it serves as a multiple oxide which these oxides combined with the element of further others. On the other hand, when qualification ingredients are compounds other than the oxide of at least one element of Ti, Zr, Hf, Nb, Ta, Cr, Mo, and W, a surface modulator serves

as a multiple oxide which the oxide of the above-mentioned element or the above-mentioned element combined with the element of further others, and oxygen.

[0056]

Moreover, in addition to the above-mentioned element and oxygen, as a multiple oxide of at least one element chosen from Ti, Zr, Hf, Nb, Ta, Cr, Mo, and W, the multiple oxide containing nickel and/or Li can be mentioned, nickel and/or Li are contained because possibility that a qualification ingredient and the lithium nickel complex oxide which has nickel and Li will react in a baking process is high. It is the multiple oxide of at least one element with which a desirable multiple oxide is chosen from a viewpoint of the stability of a compound by Ti, Zr, Hf, Nb, Ta, Cr, Mo, and W, oxygen, and Li. Specifically as such a multiple oxide, LiNbO_3 , LiTaO_3 , Li_3TaO_4 , Li_4TiO_4 , Li_2TiO_3 , and Li_3NbO_4 grade can be mentioned.

[2] Positive active material, a positive-electrode ingredient, and a lithium secondary battery

The surface qualification lithium nickel complex oxide manufactured as mentioned above is used as positive active material of a lithium secondary battery. A lithium secondary battery has the cell element which usually has the positive electrode containing positive active material, a negative electrode, and an electrolyte, and the case which contains said cell element.

[0057]

A positive electrode usually comes to form a positive-electrode ingredient layer on a charge collector, and said positive-electrode ingredient layer consists of positive-electrode ingredients. Into this positive-electrode ingredient, occlusion, the positive active material which may be emitted and the below-mentioned binder, electric conduction material, etc. contain Li. In this invention, surface qualification lithium nickel complex oxide is used as positive active material. While lithium nickel complex oxide has the advantage to which the current capacity per unit weight becomes large, it is inferior to thermal stability and has the problem that the impedance of a lithium secondary battery will rise at the time of elevated-temperature preservation. In this invention, the above-mentioned impedance rise can be controlled now by embellishing a lithium-nickel-complex-oxide front face with the compound of predetermined periodic-table 4B - 6B group element.

[0058]

As positive active material, although surface qualification lithium nickel complex oxide may be used independently, you may use together with other lithium transition-metals multiple oxides. A lithium cobalt multiple oxide

can be mentioned as such a lithium transition-metals multiple oxide. A lithium cobalt multiple oxide is an oxide which contains a lithium and cobalt at least. Since the lithium cobalt multiple oxide has the flat discharge curve, it is a useful positive-electrode ingredient which is excellent in a rate property. As a lithium cobalt multiple oxide, the LiCoO₂ grade which has the layer structure can be mentioned, for example. Moreover, a lithium cobalt multiple oxide may permute a part of site which Co occupies by elements other than Co. By permuting Co site by other elements, the cycle property and the rate property of a cell may improve, as a permutation element at the time of elements other than Co permuting a part of site which Co occupies, Ti, aluminum, Ti, V, Mn, Li, nickel, Cu, Zn, Mg, Ga, Sb, germanium, etc. mention -- having -- desirable -- Ti, aluminum, Li, nickel, Mg, Ga, Sb, and germanium -- furthermore, they are Ti, aluminum, and Mg preferably. In addition, Co site may be permuted by two or more sorts of other elements.

[0059]

the case where a permutation element permutes Co site -- the rate -- usually -- more than 0.03 mol % of Co element -- desirable -- more than 0.05 mol % -- it is -- usually -- less than [of Co element / 30 mol %] -- it is less than [20 mol %] preferably. If many [if there are too few permutation rates, the improvement in stability of the crystal structure may not be enough, and / too], the capacity at the time of making it a cell may fall.

[0060]

Although a lithium cobalt multiple oxide is usually expressed with LiCoO₂ as a fundamental presentation before charge, as described above, it may permute a part of Co site by other elements. Moreover, in the above-mentioned empirical formula, there may be a little oxygen deficiency and indeterminate nature and a part of oxygen site may be permuted by sulfur or the halogen. Furthermore, in the above-mentioned empirical formula, the amount of lithiums can be made superfluous or lack.

[0061]

The specific surface area of a lithium cobalt multiple oxide is more than 0.4m²/g more preferably, and is below 2.0m²/g below 5.0m²/g below 10m²/[of usual] g more than 0.1m²/g preferably more than 0.01m²/[of usual] g. If specific surface area is too small, the fall of a rate property and the fall of capacity will be caused, if too large, the electrolytic solution etc. and the reaction which is not desirable will be triggered, and a cycle property may be reduced. Measurement of specific surface area follows a BET adsorption method.

[0062]

The description of a lithium cobalt multiple oxide is usually fine particles in ordinary temperature normal relative humidity (25 degrees C / 50%RH), and it is common that it is in the condition of the primary particle of the diameter of a granule having condensed and having formed the aggregated particle. And 100 micrometers or less 50 micrometers or less are 20 micrometers or less most preferably still more preferably usually preferably [this second / an average of / particle size is usually desirable 0.1 micrometers or more, and 0.2 micrometers or more 0.3 micrometers or more are 0.5 micrometers or more most preferably still more preferably, and] 300 micrometers or less. If cycle degradation of a cell may become large if the second [an average of] particle size is too small, or a problem may arise at safety and it is too large, the internal resistance of a cell becomes large and it may be hard coming to come out an output.

[0063]

Although especially both weight ratio is not restricted when using together surface qualification lithium nickel complex oxide and a lithium cobalt multiple oxide, on the other hand, the rate of surface qualification lithium nickel complex oxide to the AUW of surface qualification lithium nickel complex oxide and a lithium cobalt multiple oxide is usually 99 or less % of the weight usually 90 or less % of the weight preferably 40% of the weight or more 1% of the weight or more. The effectiveness of this invention is notably demonstrated by considering as the above-mentioned range.

[0064]

As positive active material which can be used together with lithium nickel complex oxide in addition to a lithium cobalt multiple oxide, various kinds of inorganic compounds, such as transition-metals oxide, various kinds of lithium transition-metals multiple oxides other than the above-mentioned lithium cobalt multiple oxide, and a transition-metals sulfide, can mention, Fe, Mn, etc. are used as transition metals here. concrete — MnO and V2 O5 V6 O13 and TiO2 etc. — the multiple oxide powder of lithiums, such as transition-metals oxide powder and a lithium manganese multiple oxide, and transition metals, and TiS2 FeS and MoS2 etc. — transition-metals sulfide powder etc. is mentioned. These compounds may carry out an element permutation partially in order to raise the property. Moreover, organic compounds, such as the poly aniline, polypyrrole, the poly acene, a disulfide system compound, a polysulfide system compound, and N-fluoro pyridinium salt, can also be used together. Naturally these inorganic compounds and an organic compound may be mixed and used together. 1-30 micrometers of particle size of the active material of these positive electrodes are usually preferably set to 1-10 micrometers. Even if particle

size is too large and it is too small, it is in the inclination for cell properties, such as a rate property and a cycle property, to fall.

[0065]

The negative electrode used for the lithium secondary battery of this invention comes to form a negative-electrode ingredient layer on a charge collector, and usually contains occlusion and the negative-electrode active material which may be emitted for Li in said negative-electrode ingredient layer.

A carbon system active material can be mentioned as a negative-electrode active material. As a carbon system active material, although the carbide of a graphite and coal system corks, petroleum system corks, and a coal system pitch, the carbide of a petroleum system pitch, or these pitches were oxidized, the carbon material which graphitized a part of these, furnace black, acetylene black, a pitch based carbon fiber, etc. can be used for lists, such as carbide, such as carbide, needle coke, pitch coke, phenol resin, and crystalline cellulose, for example. Moreover, these carbon system active material can be used even if it is the form of a mixture with a metal, or the salt and an oxide, and a covering object. As a negative-electrode active material besides the above-mentioned carbon system active material, metals, such as lithium alloys, such as a metal lithium, Li-aluminum, Li-Bi-Cd, and Li-Sn-Cd, a lithium transition-metals nitride, a silicon, and tin, etc. can be used for oxide, such as a silicon, tin, zinc, manganese, iron, and nickel, or a sulfate pan. 1-50 micrometers of particle size of these negative-electrodes active material are usually 5-30 micrometers preferably. Even if too large and too small, it is in the inclination for cell properties, such as initial effectiveness, a rate property, and a cycle property, to fall. Of course, two or more sorts of negative-electrode active materials chosen from from while describing above may be used together.

[0066]

In a positive-electrode ingredient layer and a negative-electrode ingredient layer, the binder other than the above-mentioned positive active material and a negative-electrode active material may be contained. the case of the binder to the active material 100 weight section -- usually -- more than the 0.01 weight section -- desirable -- more than the 0.1 weight section -- further -- desirable -- more than 1 weight section -- usually -- they are below 15 weight sections still more preferably below 30 weight sections preferably below 50 weight sections. When there are too few amounts of a binder, a firm positive electrode cannot make it form easily. If there are too many amounts of a binder, energy density and a cycle property may

fall.

[0067]

As a binder, for example Alkane system polymer; polybutadienes, such as polyethylene, polypropylene, Polly 1, and 1-dimethyl ethylene, Partial saturation system polymers, such as polyisoprene; Polystyrene, poly methyl styrene, The polymer which has rings, such as polyvinyl pyridine and Polly N-vinyl pyrrolidone; A polymethyl methacrylate, Polymethacrylic acid ethyl, polymethacrylic acid butyl, polymethylacrylate, Acrylic derivative system polymers, such as polyacrylic acid ethyl, polyacrylic acid, polymethacrylic acid, and polyacrylamide; Pori vinyl fluoride Fluororesin, such as polyvinylidene fluoride and polytetrafluoroethylene; A polyacrylonitrile, CN radical content polymers, such as the poly vinylidene cyanide; Polyvinyl acetate, Polyvinyl alcohol system polymers, such as polyvinyl alcohol; various kinds of resin, such as conductive polymers, such as halogen content polymer; poly anilines, such as a polyvinyl chloride and a polyvinylidene chloride, can be used. Moreover, it can be used even if it is mixture, such as the above-mentioned polymer, a conversion object, a derivative, a random copolymer, an alternating copolymer, a graft copolymer, a block copolymer, etc. Moreover, silicate and an inorganic compound like glass can also be used. In this invention, it is desirable to use fluororesin, such as the Pori vinyl fluoride, polyvinylidene fluoride, and polytetrafluoroethylene.

[0068]

The weight average molecular weight of a binder is 20000 or more still more preferably, and is usually [1000 or more] 300000 or less still more preferably 1 million or less preferably usually [5 million or less] 10000 or more. If too low, the reinforcement of a paint film falls and is not desirable. If too high, viscosity will become high and formation of an active material layer will become difficult.

[0069]

Moreover, in a positive-electrode ingredient layer and a negative-electrode ingredient layer, the additive which discovers various kinds of functions, such as an electrical conducting material and reinforcing materials, if needed, fine particles, a filler, etc. may be contained. Although there will be especially no limit if optimum dose mixing is carried out and conductivity can be given to the above-mentioned active material as an electrical conducting material, carbon powder, such as acetylene black, carbon black, and a graphite, various kinds of metal fibers, a foil, etc. are usually mentioned. As reinforcing materials, inorganic [various kinds of], an organic globular shape, a fibrous filler, etc.

can be used.

[0070]

As an ingredient of the charge collector used for a positive electrode and a negative electrode, the alloy of metals, such as aluminum, copper, nickel, tin, and stainless steel, and these metals etc. can usually be used. In this case, as a charge collector of a positive electrode, aluminum is usually used and copper is usually used as a charge collector of a negative electrode. Especially the configuration of a charge collector is not restricted, for example, can mention tabular and a mesh-like configuration. 1-50 micrometers of thickness of a charge collector are usually 1-30 micrometers preferably. Although a mechanical strength will become weak if too thin, if too thick, a cell will become large, the tooth space occupied in a cell becomes large, and the energy density of a cell becomes small.

[0071]

The thickness of a positive electrode and a negative electrode is 10 micrometers or more preferably, and is usually 200 micrometers or less preferably 500 micrometers or less 1 micrometers or more, respectively. Even if too thick and thin, it is in the inclination for cell engine performance, such as capacity and a rate property, to fall.

In the manufacture approach of a positive electrode and a negative electrode, especially a limit can apply to a charge collector the slurry which made the solvent contain the positive-electrode ingredient for lithium secondary batteries which consists of a binder which there is not, for example, is used an active material and if needed, electric conduction material, etc., and can manufacture it by drying. Moreover, for example, it can also manufacture by being stuck to a charge collector by pressure after kneading positive-electrode ingredients for lithium secondary batteries used an active material and if needed, such as a binder and electric conduction material, without using a solvent.

[0072]

The electrolyte used for the lithium secondary battery of this invention usually contains a solute and a nonaqueous solvent (in this specification, a solute and a nonaqueous solvent may be set and it may be called the electrolytic solution or nonaqueous electrolyte).

any of lithium salt conventionally well-known as a solute -- although -- it can be used. For example, LiClO₄, LiAsF₆, LiPF₆, LiBF₄, LiB(C₆H₅)₄, CH₃SO₃Li, CF₃SO₃Li, LiN(SO₂CF₃)₂, LiN(SO₂C₂F₅)₂, LiC(SO₂CF₃)₃, LiSbF₆, LiSCN etc. is mentioned and at least one or more sorts of things can be used among these. From the point that the effectiveness of this invention becomes remarkable among these to LiClO₄, LiPF₆ it is especially desirable.

The content to the nonaqueous electrolyte of these solutes is usually 0.5 - 2.5 mol/l.

[0073]

As a nonaqueous solvent, one sort or two sorts or more of mixture, such as nitril, such as lactone, such as ether, such as furans, such as un-annular carbonate, such as annular carbonate, such as ethylene carbonate, propylene carbonate, and vinylene carbonate, dimethyl carbonate, diethyl carbonate, and ethyl methyl carbonate, a tetrahydrofuran, and 2-methyl tetrahydrofuran, and dimethoxyethane, and gamma-butyl lactone, and an acetonitrile, can be mentioned, for example. Among these, one sort or two sorts or more of mixed solutions chosen from annular carbonate, un-annular carbonate, and lactone are desirable.

[0074]

It is more desirable that the boiling point in 20 degrees C / 1 atmospheric pressure makes a nonaqueous solvent contain a high-boiling point solvent 150 degrees C or more in this invention from a viewpoint which secures the stability of the electrolyte at the time of elevated-temperature preservation. Although the above-mentioned high-boiling point solvent means the solvent which is usually in the range whose boiling point is 150 degrees C - 300 degrees C, it is a solvent which has 180 degrees C - 270 degrees C of boiling points in the range whose boiling point is 200 degrees C - 250 degrees C preferably. By using the solvent which has the boiling point of the above-mentioned range, the thermal stability at the time of elevated-temperature preservation of a cell can be raised more certainly. As such a solvent, ethylene carbonate (243 degrees C of boiling points), propylene carbonate (240 degrees C of boiling points), gamma-butyrolactone (204 degrees C of boiling points), etc. can be mentioned, for example. These high-boiling point solvent may be used independently, and plurality may be used together, and it may use together with a low-boiling point solvent (in this invention, the boiling point says a thing 150 degrees C or less.) further, and you may use. In addition, "the boiling point in 20 degrees C / 1 atmospheric pressure is X degrees C or more" means that vapor pressure does not exceed one atmospheric pressure even if it heats from 20 degrees C to X degrees C under pressure 1 atmospheric pressure.

[0075]

In addition, nonaqueous electrolyte may contain further the additive for securing the safety and cell property (for example, cycle property) other than the above-mentioned solute and a nonaqueous solvent.

As for the above-mentioned electrolyte, it is desirable to infiltrate the spacer which may be arranged between a positive electrode, a negative

electrode, and a positive electrode and a negative electrode for improvement in the ionic conductivity by the lithium ion, respectively. [0076]

A spacer is usually used in order to prevent the short circuit between a positive electrode and a negative electrode. A spacer usually consists of porous film. As an ingredient used as a spacer, the porous film of resin, such as polyolefines, such as polyethylene and polypropylene, and polyolefines by which a part or all of these hydrogen atoms was permuted by the fluorine atom, a polyacrylonitrile, polyaramide, is mentioned, for example. From the point of stability over the point of the chemical stability to an electrolyte, and the electrical potential difference impressed, preferably, it is polyolefine or the polyolefine by which the fluorine permutation was carried out, and, specifically, that by which a part or all of polyethylene, polypropylene, and these hydrogen atoms was permuted by the fluorine atom can be mentioned. Also in these, especially preferably, it is polyolefines, such as polyethylene and polypropylene, polytetrafluoroethylene (PTFE), and polyvinylidene fluoride, and they are polyolefines, such as polyethylene and polypropylene, most preferably. Of course, such copolymers and mixture can also be used. [0077]

The lithium secondary battery of this invention usually comes to contain a cell element in a case. A cell element is formed on the basis of the unit cell element which usually consists of the positive electrode and negative electrode which use an active material as a principal component, and an electrolyte, forms this unit cell element in a long picture, and is formed by rolling this about or carrying out two or more laminatings of this unit cell element formed in plate-like. That is, as a gestalt of a cell element, the monotonous laminating mold which carried out two or more sheet laminating of the plate-like unit cell element, the plate-like winding mold which wound the unit cell element which formed in the long picture so that it might become plate-like, and the cylinder winding mold which wound further the unit cell element formed in the long picture in the shape of a cylinder can be mentioned, for example. As for the gestalt of productivity and the point which can be miniaturized to a cell element, in this invention, it is desirable that they are a plate-like winding mold or a monotonous laminating mold. [0078]

In the lithium secondary battery of this invention, the case which contains a cell element can mention metal casings, such as a product made from SUS (stainless steel), and the case where it has configuration variability.

Since rigidity of metal casing is high, while it has the advantage which can secure the safety of a lithium secondary battery now enough, since weight is heavy, there is a disadvantageous point of being unsuitable in the cell of a portable electrical machinery and apparatus. Since the case where it, on the other hand, has the configuration variability which consists of a laminate film etc. has the thin thickness of a case, while it has the advantage whose lightweight-ization is attained, since rigidity is low, it has the disadvantageous point that the opposite impact nature of a lithium secondary battery is inferior. That is, what is necessary will be just to choose the class of the above-mentioned case by the application for which a lithium secondary battery is used.

[0079]

When using a lithium secondary battery as a power source of an electrical machinery and apparatus which is carried as above-mentioned, it is desirable to use the case where it has configuration variability. As an ingredient of a configuration variability case, metals, such as aluminum, iron which carried out nickel plating, and copper, synthetic resin, etc. can be used. Preferably, they are the laminate film which comes to prepare a gas barrier layer and a resin layer, and the laminate film with which the resin layer was especially prepared in both sides of a gas barrier layer. Such a laminate film has high configuration variability and thinness while having high gas barrier property. Consequently, thin-film-izing and lightweight-ization of a sheathing material can be attained, and the capacity as the whole cell can be raised.

[0080]

As an ingredient of the gas barrier layer used for a laminate film, metallic oxides, such as alloys, such as metals and stainless steel, such as aluminum, iron, copper, nickel, titanium, molybdenum, and gold, and Hastelloy, silicon oxide, and an aluminum oxide, can be used. Preferably, it is lightweight and is aluminum which is excellent in workability.

As resin used for a resin layer, various kinds of synthetic resin, such as thermoplastics, thermoplastic elastomer, thermosetting resin, and a plastic alloy, can be used. That with which fillers, such as a filler, are mixed is also included in these resin.

[0081]

the thickness of a configuration variability case — usually — 0.01 micrometers or more — desirable — 0.02 micrometers or more — further — desirable — 0.05 micrometers or more — it is — usually — 0.15mm or less costs 0.2mm or less most preferably still more preferably 0.3mm or less still more preferably 0.5mm or less 1mm or less. It can carry out [small

and lightweight]-izing of the cell more so that it is thin, but if too thin, the danger that a case will explode by the generation of gas at the time of elevated-temperature preservation not only becomes large, but sufficient rigid grant becomes impossible or sealing nature may fall.

[0082]

The thickness of the whole lithium secondary battery with which a case comes to contain a cell element is 5mm or less usually 4mm or less still more preferably 4.5mm or less preferably. Especially the effectiveness of this invention is large to such a thin lithium secondary battery. However, since a too much thin cell has a too small capacity or is difficult to manufacture, it is 0.5mm or more usually 2mm or more still more preferably 1mm or more preferably.

[0083]

In addition, since facilities, such as wearing to the device of a cell, are given, a cell element is enclosed with a configuration variability case, and it is [after fabricating in a desirable configuration] also possible to contain the lithium secondary battery of these plurality in the sheathing case which has rigidity further if needed.

As an electrical machinery and apparatus with which the lithium secondary battery of this invention is used as a power source For example, a portable personal computer (in this specification, a personal computer may only be called personal computer) A pen input personal computer, a mobile personal computer, an Electronic Book player, a cellular phone and a cordless phon — a cordless handset, a pager, and a handy terminal — Pocket facsimile, a pocket copy, a pocket printer, a headphone stereo, A video movie, a liquid crystal television, a handy cleaner, portable CD, A mini disc, an electric shaver, a transceiver, an electronic notebook, a calculator, Memory card, a pocket tape recorder, radio, a backup power supply, a motor, a luminaire, a toy, a game device, a load conditioner, a clock, a stroboscope, a camera, medical equipment (a pace maker, hearing aid, and a shoulder are also **** etc.), etc. can be mentioned. Moreover, the lithium secondary battery of this invention can also be used as a power source for electric vehicles.

[0084]

Hereafter, the concrete configuration of the lithium secondary battery of this invention is explained by making into an example the lithium secondary battery by which sealing receipt was carried out in the configuration variability case in the cell element of a monotonous laminating mold. However, these are one example to the last, and it cannot be overemphasized that it is not what is limited to these modes.

[0085]

[Example]

(b) Manufacture of a positive-electrode agent

[Manufacture of the positive-electrode agent 1]

the diameter of an aggregated particle — 10 micrometers (primary particle size: 1 micrometer) lithium-nickel-complex-oxide: —

$\text{LiNi}_{0.82}\text{Co}_{0.15}\text{Al}_{0.03}\text{O}_2$ was used. This lithium nickel complex oxide and the niobium oxide sol (Taki Chemical [Co., Ltd.] Co., Ltd. make) by which niobium oxide was distributed in the solvent were made to react, and Nb compound surface qualification lithium nickel complex oxide was manufactured.

[0086]

Weighing capacity of the niobium oxide sol is carried out to 300ml beaker, and specifically, the acetone was evaporated, putting in and agitating lithium nickel complex oxide, after putting in about 50ml of acetones and agitating and distributing them. It heated in 120-degree-C oven, and was made to harden by drying completely finally. Since the mixture of the niobium oxide sol after desiccation and lithium nickel complex oxide was condensed, it broke this down lightly with the medicine spoon, and made it the shape of fine particles. The obtained mixed powder was put into the baking pan made from an alumina, and Nb surface qualification lithium nickel complex oxide was obtained by calcinating in an oxygen air current for 500 degree-Cx 6 hours.

[0087]

in addition, a niobium oxide sol — niobium oxide — 20Nb5 conversion — 10wt(s)% — since it was what is contained, in case weighing capacity of the niobium oxide sol is carried out to 300ml beaker, the amount of a niobium oxide sol is controlled, and the amount of a niobium oxide sol was made to become 10wt% 1wt% to lithium nickel complex oxide, respectively That is, the niobium oxide throughput to lithium nickel complex oxide manufactured two kinds of surface qualification lithium nickel complex oxide which is 1wt% 0.1wt(s)%.

[0088]

Thus, the obtained positive-electrode agent from which niobium oxide throughput differs is called as shown in Table -1.

[0089]

[Table 1]

[表-1]

酸化ニオブの表面修飾量 (wt %)	正極剤の名称
0 (未処理)	正極材 1 a
0.1	正極剤 1 b
1	正極剤 1 c

[0090]

[Manufacture of the positive-electrode agent 2]

In manufacture of the positive-electrode agent 1, the positive-electrode material 2 was manufactured like manufacture of the positive-electrode material 1 except having made the niobium oxide sol into the titanium oxide sol (Taki Chemical [Co., Ltd. / Co., Ltd.] make: tie knock M-6).

In addition, because of the thing containing 6wt% TiO₂, in case the above-mentioned titanium oxide sol carries out weighing capacity of the titanium oxide sol to 300ml beaker, it controls the amount of a titanium oxide sol, and the amount of a titanium oxide sol was made to become 10wt% 1.0wt(s)% to lithium nickel complex oxide. That is, the titanium oxide throughput to lithium nickel complex oxide manufactured two kinds of surface qualification lithium nickel complex oxide which is 0.6wt% 0.06wt(s)%.

[0091]

Thus, the obtained positive-electrode agent from which titanium oxide throughput differs is called as shown in Table -2.

[0092]

[Table 2]

[表-2]

酸化チタンの仕込量 (wt %)	正極剤の名称
0.06	正極剤 2 a
0.6	正極剤 2 b

[0093]

(b) Manufacture of a positive electrode, a negative electrode, and the electrolytic solution

[Manufacture of a positive electrode]

The positive electrode was manufactured using the positive-electrode agents 1a, 1b, 1c, and 2a and 2b which were obtained as mentioned above. The approach is shown below.

First, the following presentations were kneaded with the planetary mixer type kneading machine for 2 hours, and the positive-electrode coating was manufactured.

[0094]

[Table 3]

Positive-electrode agent (*) 85 weight sections

Acetylene black Ten weight sections

Pori fluoride kinky thread NIDEN Five weight sections

N-methyl-2-pyrrolidone 80 weight sections

* ... That it is with a positive-electrode agent shows the positive-electrode agents 1a, 1b, 1c, and 2a and 2b, respectively.

[0095]

Next, on the aluminum charge collector base material of 15-micrometer thickness, it applied by die coating of an extrusion die, the above-mentioned positive-electrode coating was dried, and the positive-electrode ingredient layer with which the active material was bound on the charge collector with the binder was manufactured. Subsequently, it was with the roll press (calender) and the electrode sheet was manufactured by carrying out consolidation. Then, the electrode was cut down from the electrode sheet and it considered as the positive electrode.

[Manufacture of a negative electrode]

The following presentations were kneaded with the planetary mixer type kneading machine to the beginning for 2 hours, and were used as the negative-electrode coating at it.

[0096]

[Table 4]

Graphite (particle size of 15 micrometers) The 90 sections

Polyvinylidene fluoride The ten sections

N-methyl-2-pyrrolidone The 100 sections

Next, the above-mentioned negative-electrode coating was applied by die coating of an extrusion die on the copper charge collector base material of 20-micrometer thickness, it dried, and the negative-electrode ingredient layer with which the active material was bound on the charge collector with the binder was manufactured. Subsequently, the electrode sheet was produced by carrying out consolidation using a roll press (calender). Then, the electrode was cut down from the electrode sheet and

it considered as the negative electrode.

[The ratio of a positive electrode and a negative-electrode ingredient layer]

In manufacture of the above-mentioned positive electrode 1, a positive electrode 2, and a negative electrode, the thickness of a positive-electrode ingredient layer and a negative-electrode ingredient layer was adjusted so that it might be set to (the charge capacity of a positive electrode) / (charge capacity of a negative electrode) = 0.93. Here, charge capacity of a negative electrode was based on the capacity (mAh/g) per negative-electrode unit volume when charging to 1.5V-3mV using a counter electrode Li.

[Manufacture of the electrolytic solution]

The mixed liquor (volume ratio EC:DMC:EMC=30:35:35) of the ethylene carbonate (EC) which dissolved LiPF₆ of 1 M concentration as lithium salt, dimethyl carbonate (DMC), and ethyl methyl carbonate (EMC) was used as the electrolytic solution.

(c) Manufacture of a lithium secondary battery

The laminating of the positive electrode and negative electrode which were prepared as mentioned above was carried out through the separator made from a macromolecule porosity film, the lead wire which takes out a current to the electrode terminal area of a positive electrode and each negative electrode further was connected, and the cell layered product was manufactured.

[0097]

In this way, the electrolytic solution was poured in after holding the laminate film which covered both sides of the aluminum film with the resin layer for the obtained cell layered product in the saccate case which carried out opposite shaping, and the electrolytic solution was infiltrated into the positive electrode, the negative electrode, and the separator. The seal section except the side which sandwiched the electrode terminal area on the tape made from polyethylene of two sheets (short circuit prevention of a terminal area sake), and took out lead wire after obturation with the reduced pressure seal was bent so that a cell sheathing-material side face might be met. The bent seal section was pasted up on the sheathing-material encapsulation section side face with commercial epoxy system adhesives. The lithium secondary battery was manufactured as mentioned above.

(d) Evaluation of a lithium secondary battery

[Cell volumetry]

Since the capacity per unit weight of LiNi_{0.82}Co_{0.15}aluminum 0.0302 which

is the positive active material of each lithium secondary battery was 185 mAh/g, 1C' per 1g of positive active material was set to 185mA, the discharge capacity of each lithium secondary battery was measured as follows, and the value of "original" 1C of each lithium secondary battery was calculated. That is, constant-potential charge was performed after charging to 4.2V in the constant current of a 25-degree C basis and 0.5C' x (positive-active-material weight) until the current value declined to 25mA in 4.2V. Then, the capacity at the time of discharging to 2.7V in the constant current of 0.2C' x (positive-active-material weight) was measured, and this was made into the discharge capacity alpha of a lithium secondary battery. And 1C (mA) of each lithium secondary battery was decided from the discharge capacity alpha (mAh) obtained by doing in this way.

[0098]

It performed constant-potential charge after charging to 4.2V in a 25-degree C basis and 0.5CmA constant current until the current value decreased the cell capacity of each lithium secondary battery to 25mA in 4.2V. Then, the capacity at the time of performing constant-current discharge to 2.7V by 0.2CmA was measured, and this was made into the cell capacity of each lithium secondary battery.

[Rate property measurement]

Constant-potential charge was performed after charging each lithium secondary battery to 4.2V in a 25-degree C basis and 0.5CmA constant current until the current value declined to 25mA in 4.2V.

[0099]

Then, constant-current discharge was performed to 2.7V at 6C discharge rate, and the rate of the obtained discharge capacity and the 0.2C discharge rate capacity obtained by the above [cell volumetry] was made into the rate property.

[Impedance measurement]

solartron SI made from instruments 1287 Electrochemical Interface and company SI 1260 Impedance/Gain-Phase Analyzer The combined equipment is used. The 25-degree C basis and the impedance of each lithium secondary battery charged to 4.2V were measured in 25 degrees C and a field with a frequency of 100kHz - 0.01Hz.

[Cycle property measurement]

After charging by performing constant-potential charge until the current value declined to 25mA in 4.2V after carrying out constant-current charge of each lithium secondary battery to 4.2V by the 25-degree C basis and 2C, it discharged by performing constant-current discharge to 2.7V by 2C. The charge and discharge of 400 cycles were performed by making this charge

and discharge into 1 cycle.

[0100]

It asked for the cycle capacity maintenance factor by calculating the capacity in 2C discharge after the 400 cycles to the capacity of 2C discharge of 1 cycle eye in each lithium secondary battery.

[Low-temperature property measurement]

Constant-potential charge was performed after charging to 4.2V in a 25-degree C basis and 0.5CmA constant current until the current value declined to 25mA in 4.2V. Then, 1CmA discharge was performed to 2.7V at 25 degrees C and -30 degrees C. The rate (discharge capacity in the discharge capacity in -30 degrees C / 25 degrees C) (x100) with a discharge capacity of -30 degrees C [to the 25-degree C discharge capacity in that case] was made into the low-temperature property.

[Elevated-temperature retention test]

Constant-potential charge was performed after charging each lithium secondary battery to 4.2V in a 25-degree C basis and 0.5CmA constant current until the current value declined to 25mA in 4.2V. And after measuring the impedance in this charge condition, the cell was put in into the 60-degree C thermostat, and after leaving it for 24 hours, it took out from the thermostat. And impedance change, remaining capacity measurement, cell volumetry after a recharge, and rate property measurement after a recharge were performed by the approach of describing below.

- Impedance change

It carried out by the approach which showed the impedance of each lithium secondary battery before an elevated-temperature retention test above [impedance measurement]. Furthermore, the impedance of the lithium secondary battery in the condition of having taken out from the thermostat was again measured after the elevated-temperature retention test.

Furthermore, constant-potential charge was performed, it considered as the charge condition, and the impedance of a lithium secondary battery was once measured in this condition until the current value decreased said lithium secondary battery to 25mA in 4.2V after discharging to 2.7V in 0.2CmA(s), and charging to 4.2V in 0.5CmA constant current again.

[0101]

each before and behind an elevated-temperature retention test -- the ratio of an impedance value, i.e., (impedance after trial)/, (impedance before a trial) was considered as impedance change. Moreover, the ratio of the impedance value before an elevated-temperature retention test and the impedance value after the recharge after an elevated-temperature retention test, i.e., (impedance after after [a trial] recharge)/, (impedance before

a trial) was considered as the impedance change after a recharge.

[0102]

In addition, about the above-mentioned impedance change, the more impedance change is close to a value [a little] smaller than 1, the more impedance change will be small. Moreover, after a recharge, the more impedance change is close to 1, the more impedance change will be small about the impedance change after the above-mentioned recharge. The reason is shown below.

[0103]

That is, if elevated-temperature preservation of the lithium secondary battery is carried out by 4.2V charge, the sag by self-discharge will occur. This sag is influenced by the difference in the class of electrolyte whether an electrolyte contains a polymer or to consist of only the electrolytic solutions again, and elevated-temperature preservation preservation conditions (a reserve time, storage temperature). The sag by this self-discharge is usually about 0.5V, when 60 degree-Cx24hrs preservation of the liquid system lithium secondary battery is carried out.

[0104]

On the other hand, the impedance value change to the charge electrical potential difference of a lithium secondary battery is as follows. Namely, the impedance value falls gradually as a charge electrical potential difference becomes gradually high from 2.7V, and as for an impedance value, a charge electrical potential difference takes the minimum value in the 4V neighborhood. An impedance rises again as a charge electrical potential difference goes up to after that and also 4.2V.

[0105]

Therefore, after elevated-temperature preservation, when there is no impedance change of the lithium secondary battery in an elevated-temperature retention test, since the fall of an impedance value occurs by the sag accompanying self-discharge, the impedance value immediately after elevated-temperature preservation turns into a value [a little] smaller than the impedance value before an elevated-temperature retention test. For this reason, about the above-mentioned impedance change, it means that impedance change is smaller as impedance change is close to a value [a little] smaller than 1.

[0106]

On the other hand, if a lithium secondary battery is charged again, an impedance value will return to a value in case a charge electrical potential difference is 4.2V. Therefore, when there is no impedance change of the lithium secondary battery in an elevated-temperature retention test, the impedance change after a recharge should be set to 1. For this reason, the

more the impedance value after a recharge is close to 1, the more impedance change will be small.

- Remaining capacity measurement

After the elevated-temperature retention test, each lithium secondary battery picked out from the thermostat was discharged to 2.7V by 0.2CmA, and the discharge capacity was made into remaining capacity. And remaining capacity (cell capacity before remaining capacity / elevated-temperature retention test) (x100) to the cell capacity before an elevated-temperature retention test was made into the rate of remaining capacity.

- Cell volumetry after a recharge (measurement of a capacity recovery factor)

After the above-mentioned remaining capacity measurement, again, constant-potential charge was performed after charging to 4.2V in 0.5CmA constant current until the current value declined to 25mA in 4.2V. Then, the capacity at the time of performing constant-current discharge to 2.7V by 0.2CmA was measured, and this was made into the cell capacity after a recharge. And cell capacity after said recharge to the cell capacity before an elevated-temperature retention test was made into the capacity recovery factor.

- The low-temperature property after a recharge

Constant-potential charge was performed after measuring a capacity recovery factor and charging to 4.2V in a 25-degree C basis and 0.5CmA constant current until the current value declined to 25mA in 4.2V. Then, 1CmA discharge was performed to 2.7V at 25 degrees C and -30 degrees C. The rate (discharge capacity in the discharge capacity in -30 degrees C / 25 degrees C) (x100) with a discharge capacity of -30 degrees C [to the 25-degree C discharge capacity in that case] was made into the low-temperature property after a recharge.

(**) Examples 1 and 2, the example 1 of a comparison

Below, five kinds of lithium secondary batteries manufactured above "manufacture of a lithium secondary battery (Ha)" were divided into examples 1 and 2 and the example 1 of a comparison, as shown in Table -3. [0107]

[Table 5]

[表-3]

実施例 1

酸化ニオブの仕込量 (w t %)	正極剤の名称
0.1	正極剤 1 b
1	正極剤 1 c

実施例 2

酸化チタンの仕込量 (w t %)	正極剤の名称
0.06	正極剤 2 a
0.6	正極剤 2 b

比較例

酸化ニオブゾルの仕込量 (w t %)	正極剤の名称
0	正極剤 1 a

[0108]

Cell capacity, a rate property, a cycle property, and low-temperature output characteristics were measured according to the above [cell volumetry], [rate property measurement], [cycle property measurement], and [low-temperature property measurement], respectively about each lithium secondary battery of examples 1 and 2 and the example 1 of a comparison. A measurement result is shown in Table -4. Furthermore, according to the above [an elevated-temperature retention test], impedance change, the impedance change after a recharge, the rate of remaining capacity, the capacity recovery factor, and the low-temperature property after a recharge were measured, respectively about each lithium secondary battery of examples 1 and 2 and the example 1 of a comparison. A measurement result is shown in Table -5.

[0109]

[Table 6]

表-4

	酸化ニオブ仕込み量(wt%)	容量率(mAh)	レート特性(%)	サイクル特性(%)	低温特性(%)
実施例1	0.1	14.4	82.7	98.2	65.8
	1	14.6	80.0	97.3	62.2
比較例	0	14.6	83.8	94.6	69.5

	酸化タンタル仕込み量(wt%)	容量率(mAh)	レート特性(%)	サイクル特性(%)	低温特性(%)
実施例2	0.06	14.6	84.4	95.7	66.4
	0.6	14.6	83.7	95.9	64.9

表-5

室温保存経時					
	酸化ニオブ仕込み量(wt%)	インピーダンス変化	再充電後のインピーダンス変化	容量回復率(%)	再充電後の低温特性(%)
実施例1	0.1	2.42	1.94	93.7	38.1
	1	1.07	1.08	94.3	39.6
比較例	0	2.59	2.47	93.1	36.2

	酸化タンタル仕込み量(wt%)	インピーダンス変化	再充電後のインピーダンス変化	容量回復率(%)	再充電後の低温特性(%)
実施例2	0.06	1.92	1.75	96.3	38.9
	0.6	1.20	1.13	97.5	40.2

By embellishing a lithium-nickel-complex-oxide front face with a niobium oxide sol or a titanium oxide sol from Table -5 as compared with unsettled lithium nickel complex oxide (example 1 of a comparison) shows that the

low-temperature property after impedance change, impedance change of a recharge, and the recharge after an elevated-temperature retention test is improved. It turns out that impedance change and the impedance change after a recharge become good as the charge of a niobium oxide sol or a titanium oxide sol increases especially. Moreover, the rate of remaining capacity and a capacity recovery factor are ***** or ** which hardly changes also with the surface qualification with niobium oxide or titanium oxide, or is improved rather.

[0110]

On the other hand, although it falls a little from Table -4 as the charge of a low-temperature property of a niobium oxide sol or a titanium oxide sol increases, the amount of falls will not have almost effect, if real use is taken into consideration.

Moreover, as for cell capacity, a rate property, and a cycle property, Table -4 shows that the surface qualification with niobium oxide and titanium oxide is hardly influenced, either.

[0111]

As mentioned above, in this invention, it turns out that the stability at the time of elevated-temperature preservation, especially impedance change are improvable by leaps and bounds, without spoiling most of the basic property of cells, such as cell capacity, a rate property, and a cycle property, if the front face of lithium nickel complex oxide is embellished with niobium oxide or titanium oxide.

Moreover, table - 4 and 5 also show that what is necessary is to be used under hot environments in many cases, to make [many] the charge of a niobium oxide sol or a titanium oxide sol in a lithium secondary battery which thinks more making small impedance change at the time of elevated-temperature preservation etc. as important although a low-temperature property is reduced a little, and just to improve stability at the time of elevated-temperature preservation.

[0112]

[Effect of the Invention]

According to this invention, after making the compound of the predetermined element whose melting point of the oxide of said element is 750 degrees C or more among periodic-table 4B - 6B group's elements exist on the surface of lithium nickel complex oxide, the high lithium nickel complex oxide of thermal stability can be obtained by using the surface qualification lithium nickel complex oxide manufactured by calcinating said lithium nickel complex oxide.

[0113]

The positive-electrode ingredient and lithium secondary battery which are excellent in the stability at the time of elevated-temperature preservation can be obtained without spoiling the fundamental property of lithium secondary batteries, such as cell capacity, a rate property, a cycle property, and a low-temperature property, by using the above-mentioned surface qualification lithium nickel complex oxide as positive active material of a lithium secondary battery especially.

further -- the above -- the manufacture approach of surface qualification lithium nickel complex oxide that a highly efficient lithium secondary battery is offered can also be acquired.

[Translation done.]